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melampyrin. As will be evident by-and-bye, we likewise fix upon the formula $C_6H_{14}O_6$, but we think it will be conceded that the method which we are adopting is calculated to furnish results of higher certainty than that followed by Gilmer. Here are three iodides corresponding to the three probable formulæ for melampyrin:—

	$C_5H_{11}I$	$C_6H_{13}I$	$C_7H_{15}I$
C	30·30	33·96	37·17
H	5·56	6·13	6·64
I	64·14	59·91	56·19
	100·00	100·00	100·00

The carbon-difference is, as will be observed, between 3 and 4 per cent. Furthermore, there is a wide difference between the boiling points of these iodides; and from each one, derivatives may be got which present all manner of physical differences.

But there is another particular to which we would direct attention. Gilmer's baryta-derivative can, at the utmost, only establish that the molecular weight of melampyrin requires the formula $C_6H_{14}O_6$. It leaves quite unanswered the question, is the carbon group C_6 contained in the compound? Still, the question might be proposed, has melampyrin the nature of an ether? It leaves unnegatived these formulæ, for instance:—

$$C_6H_{14}O_6 = \left.\begin{matrix} C_5H_8(HO)_3 \\ CH(HO)_2 \end{matrix}\right\}O \quad \ldots\ldots \quad (1)$$

$$C_6H_{14}O_6 = \left.\begin{matrix} C_4H_6(HO)_3 \\ C_2H_3(HO)_2 \end{matrix}\right\}O \quad \ldots\ldots \quad (2)$$

$$C_6H_{14}O_6 = \left.\begin{matrix} C_3H_4(HO)_3 \\ C_3H_5(HO)_2 \end{matrix}\right\}O \quad \ldots\ldots \quad (3)$$

By operating with hydriodic acid this question is at once set at rest. The obtaining of iodide of hexyl from melampyrin, not only settles the molecular weight of that substance, but also shows that the carbon-condensation is 6.

Among the rather numerous members of the mannite family we shall perhaps find some examples of the ether-formulæ just given.

The details of our experiments upon melampyrin are these. The melampyrin which we used was obtained from E. Merk, of Darmstadt, from whom we have ascertained the following particulars relative to its preparation. It was obtained from *Melampyrum nemorosum* and *M. vulgatum*.

Obviously, it was of importance to test whether it was free from mannite. For this purpose, we availed ourselves of the striking difference between the solubility of the two bodies in cold water. The solubility of mannite at 16° C. is 16 in 100 parts of water. The solubility of melampyrin, on the other hand, at the same temperature is, according to Gilmer,* 3·4 in 100 parts of water.

We made a determination of the solubility of our melampyrin in water, and also, under precisely similar circumstances, a determination of the solubility of mannite.

Inasmuch as we took care to keep the solution of melampyrin for several hours in contact with a large excess of finely powdered melampyrin, it is obvious that if our melampyrin had contained any considerable proportion of mannite, we should have got a number nearly approaching to the solubility of mannite. Nothing of the kind was observed, for these are our results:—

I. 100 parts of water at 16·5° C. dissolved 2·94 parts of melampyrin.

II. 100 parts of water at 16·5° C. dissolved 16·07 parts of mannite.

Our melampyrin was, therefore, free from mannite. It was analysed with the following results.

·3353 grm. of the substance burnt with chromate of lead and a little bichromate of potash gave ·2384 grm. of water and ·4835 grm. of carbonic acid.

	Calculated.		Found.
C_6	72 ..	39·56	39·33
H_{14}	14 ..	7·70	7·90
O_6	96 ..	52·74	
	182	100·00	

In one operation 4 grm. of melampyrin were heated in a stream of carbonic acid with 60 cub. cent. of strong hydriodic acid (boiling at 124° C). The dark-coloured oily distillate was distilled in contact with water, after having been freed from excess of iodine by means of sulphite of soda. The colourless oil which distilled weighed 2 grm.

On a larger scale the reaction did not seem to be so neat, for in

* Ann. Ch. Pharm., cxxiii, 377. In Gilmer's paper, there is a press-error, 34 instead of 3·4, with which latter number Gilmer's experiment agrees.

a second operation 20 grms. of melampyrin gave only 5·5 cub. cent. of crude iodide. The amount of hydriodic acid (boiling at 126° C.) which was used in this experiment was 230 cub. cent.

The crude iodide which distilled over was washed with sulphite of soda and then redistilled in contact with water, and in a stream of carbonic acid. After being dried with fused chloride of calcium, it could be distilled alone without much decomposition taking place. It was slightly coloured, and boiled at 165° to 175°C. (We have previously found that iodide of hexyl boils between these points.)

Analyses of our product gave these results:—

I. ·2317 grm. burnt with chromate of lead, copper-turnings being used, gave ·1320 grm. water and ·2936 grm. carbonic acid.

II. ·2338 grm. gave ·1360 grm. water and ·2982 grm. CO_2.

III. ·5790 grm. were sealed up with ethylate of sodium and heated in the water-bath for several hours. The iodide of sodium so formed was precipitated with nitrate of silver. The iodide of silver obtained weighed ·6285 grm.

	Calculated.		Found.		
			I.	II.	III.
C_6	72	33·96	34·56	34·78	
H_{13}	13	6·13	6·33	6·46	
I	127	59·91	..	..	58·66
	212	100·00			

Hence, it will be seen that the liquid was iodide of hexyl, the difference between the percentage of carbon required by iodide of hexyl and that required by iodide of heptyl being more than 3.

In order to confirm our result, we digested some of the liquid with alcoholic solution of potash for several hours; we then distilled in the water-bath, and added water to the distillate. An oil, lighter than water, and having the smell of hexylene, separated. This oil was dried with chloride of calcium, and then distilled. It boiled at 68° to 70° C. (the boiling point of hexylene); the retort was dry below 90°C. It was next saturated with bromine, with which it combined with great violence. The resulting bibromide was analysed.

I. ·2803 grm., burnt with chromate of lead and a little bichromate of potash, gave ·29·58 grm. CO_2; the water was lost.

	Calculated.			Found.
				I.
C_6	72	..	29·51	28·78
H_{12}	12	..	4·92	
Br_2	160	..	65·57	
	244		100·00	

which leaves no doubt as to the nature of the compound. Moreover, the slight deficiency of carbon was due to a trace of bromine-substitution: for at the end of the treatment, of the olefine with bromine, the escape of a trace of hydrobromic acid was noticed.

To resume. Melampyrin, free from mannite, is resolved by hydriodic acid into iodide of hexyl, according to the equation:

$$C_6H_8(HO(_6 + 11HI = C_6H_{13}I + 6H_2O + I_{10}.$$

The carbon-condensation of melampyrin is therefore the same as that of mannite. Identity between the two bodies we do not contend for; on the contrary, there is a difference in the readiness with which the reaction of hydriodic acid may be accomplished. Mannite is attacked very readily, malampyrine with greater difficulty.

A way of explaining the difference by means of formulæ, is by writing the peroxide of hydrogen in different places in the two bodies thus:

$$C_6H_8\,(HO)_6;\ C_6(HO)_6H_8$$

We do not insist upon this mode of interpretation; it is only one possible method among many.

We hope, in the course of a short time, to be able to publish an account of the various members of the sugar and mannite group. The following substances, we hope, will be ready very soon.

1. Dulcite.
2. Phycite.
3. Erythromannite.
4. Inosite.
5. Sorbite.
6. Quercite.
7. Glycogen.

The foregoing paper was nearly finished, when we read that

M. V. de Luynes had applied our method to the investigation of erythromannite. This body is particularly interesting, inasmuch as it is believed to be a mannite having the formula $C_4H_{10}O_4$, which should yield iodide of tetryl on treatment with hydriodic acid:

From M. de Luynes' communication, which appeared in the *Comptes Rendus* (Oct. 13, 1862), it seems that he boiled erythromannite with hydriodic acid, when a heavy, oily liquid distilled. This liquid, separated from the water, was redistilled several times, and then purified from excess of iodine by means of an alkali, and dried, when it boiled at 120° C. and had the composition of iodide of tetryl. We cannot pass over this notice, without remarking that it seems to us to be strange that M. de Luynes' iodide would bear the treatment to which he subjected it. Iodide of hexyl obtained from mannite would be utterly destroyed by such management; for we find that, even when freed from iodine, the crude product decomposes at low temperatures, evolving volatile liquids. It must be first distilled with water in a stream of carbonic acid; it then becomes pure and colourless, and may be dried and distilled *alone*, without decomposition. We need hardly remind M. de Luynes, that if the decomposition of which we speak did actually take place, the agreement of his analysis with the composition of iodide of tetryl, or of any other iodide, must be regarded as accidental, and as establishing nothing at all.

It is a pity that M. de Luynes did not obtain any derivative from his iodide. If he had sufficient material at command to determine the boiling point of the iodide, he must have had enough to obtain tetrylene by the action of alcoholic solution of potash. When he resumes his investigation, we would recommend him to try to get tetrylene and make the bibromide from it.

As M. de Luynes announces his intention of trying to get the other terms of the series from his iodide of tetryl, we will anticipate a portion of our history of the hexyl-compounds, which we have promised to publish when our research is tolerably complete.

Hexyl-alcohol may be prepared by heating iodide of hexyl with oxide of silver and water. There is produced, at the same time, a considerable quantity of hexylene (boiling point 70° C.), and also of another liquid of very high boiling point, most probably a *parahexylene*.

The alcohol, after repeated rectifications, boils constantly at 136° C. It is, therefore, abnormal: for 151° C. is the boiling point of the normal alcohol.

Its specific gravity at 0° C. is ·8327; it has a fragrant smell, very unlike that of amyl-alcohol. It is insoluble in water.

Mixed with concentrated sulphuric acid at 0° C it yields para-hexylene, and no trace of hexyl-sulphuric acid.

We would particularly draw attention to the fact that iodide of hexyl tends to split up into hexylene and hydriodic acid when any attempt is made to obtain compound ethers from it. With aqueous solution of caustic potash iodide of hexyl may be boiled without decomposition. With alcoholic potash or sodium-alcohol it gives hexylene. With acetate of lead, or with oxalate of silver, it gives a considerable quantity of hexylene: whether there is formed acetic or oxalic hexyl-ether, as a bye-product, we have not yet established, but we suspect it.

Heidelberg, October 21, 1862.

LIV.—*On the Separation of Tin from Antimony, and on the Analysis of Alloys containing Lead, Tin, Antimony, and Copper.*

By Charles Tookey, F.C.S.,

Of the Metallurgical Laboratory, Royal School of Mines.

The separation of tin from antimony, with a view to their direct quantitative estimation, has hitherto been regarded as an analytical process involving considerable difficulty, on account of the similarity which exists in the behaviour of the compounds of those metals with reagents.

The method proposed by Gay Lussac consists in precipitating the tin and antimony together by means of a strip of zinc; the weight of the precipitated metals having been ascertained, they are then redissolved in nitro-hydrochloric acid, and the antimony

separated from the diluted solution by a strip of tin, the amount of this metal originally associated with the antimony, being estimated by difference. The more recent method, by Rose, provides for the direct estimation of each metal, the separation being effected by fusing the oxides with hydrate of soda, and digesting the antimonate and stannate of soda produced, with diluted alcohol, the insoluble antimonate of soda being afterwards washed on a filter with alcohol of increased strength as the operation of washing approaches completion.

Having had occasion to examine some alloys containing lead, tin, and antimony, with small quantities of copper, and having failed to obtain sufficiently accurate results in the separation of tin from antimony by either of the processes mentioned, I made several attempts to effect the object in view, but without success, when the reaction between the sulphides of tin and antimony and hydrochloric acid (gas) occurred to me as likely to afford a method free from objection.

When tersulphide of antimony is exposed to the action of hydrochloric acid (gas), decomposition is effected at the ordinary temperature, with production of sulphide of hydrogen and terchloride of antimony, which, when gently heated, is easily volatilized in a current of the gas. Protosulphide of tin, when treated in a similar manner, is also decomposed, the products of decomposition being sulphide of hydrogen and proto-chloride of tin, which may be heated to incipient fusion in an atmosphere of hydrochloric acid, without undergoing any further change. A necessary condition, therefore, to the success of a separation by means of the reactions just stated, would be that the tin should exist in solution in the state of protoxide. By the method of analysis to be further described, the tin was obtained in the state of bichloride, and in endeavouring to effect the reduction of the bichloride to the state of protochloride, an experiment was made to ascertain the action of metallic iron upon the mixed chlorides of tin and antimony, in presence of an excess of hydrochloric acid, the result of which was, that while the bichloride of tin was reduced to protochloride, the whole of the antimony appeared to be separated in the metallic state.

Gmelin states, on the authority of Fischer, that iron does not precipitate tin from the protochloride at the boiling heat. To see how nearly separation could be effected by iron in the presence of

hydrochloric acid, 6·03 grs. of pure antimony and 4·16 grs. of tin were dissolved in hydrochloric acid, with addition of a few drops of nitric acid; the solution was diluted with water, and, after adding more hydrochloric acid, digested at a gentle heat with 15 grs. of thin sheet iron, until the whole of the iron was dissolved; a considerable quantity of cold water was then added, and the antimony collected on a weighed filter, after being washed with water and dried, the antimony weighed 6·02 grs. In a second experiment, 9·145 grs. of pure antimony and 1·065 grs. of pure tin were dissolved as before; the antimony in this case after drying weighed 9·18 grs., the tin was precipitated from the filtrate by sulphuretted hydrogen, the protosulphide of tin dried, and converted into binoxide by careful ignition, the amount of binoxide obtained was 1·36 grs., containing 1·069 grs. of metallic tin.

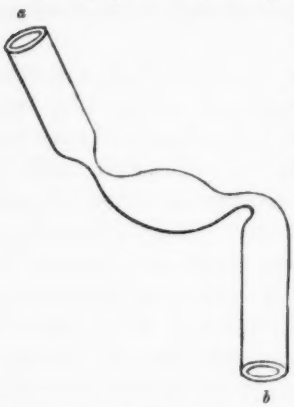
In the analyses of the alloys containing lead, tin, and antimony, with small quantities of copper, the ordinary method for separating tin and antimony from other metals was used, viz., oxidation with nitric acid, the action being promoted by heat, and the excess of acid expelled by evaporation, the nitrates of lead and copper were removed by washing on a filter with hot water. By proceeding in this manner it was found, in two analyses of the same alloy, that the amounts of lead, and also the collective weights of the oxides of tin and antimony differed to a considerable extent. The same discrepancy was observed, whether the acid used for oxidation was in the concentrated state, or previously diluted with water. In order to ascertain the source of error, the oxides of tin and antimony were examined, and found to contain oxide of lead in a state of combination, in which it could not be separated by washing with water, and to see whether the application of heat affected the result, two equal weights (10 grs.) of the same alloy were taken, one was treated in the usual manner, heat being applied to promote the oxidation by nitric acid, the excess of acid being expelled by evaporation; boiling water was then added, and after perfect washing, the mixed oxides weighed, on ignition, 8·92 grs. The other was oxidized by nitric acid, without the application of heat, and the resulting oxides weighed 7·31 grs. The application of heat causes therefore a large proportion of the lead to remain with the oxides of tin and antimony. When an alloy of lead and antimony is heated with nitric acid, the

latter metal is converted into antimonic acid, which combines with the oxide of lead, the resulting compound being insoluble in water.

That the whole of the lead might be separated from the other metals, the following process was employed. The alloy was oxidized by nitric acid, but little more acid being used than was necessary for oxidation; after removing the excess of acid by evaporation at a low temperature, the residue was digested with hot water, the oxides of tin and antimony being collected on a weighed filter, and after perfect washing, dried at 110—120° C. After ceasing to lose weight, they were carefully transferred to a glass boat; the filter with the small portion of oxides still adhering to it was again dried and weighed, the difference between the two weights giving the amount of oxides operated upon. The boat was then placed in a condensing apparatus, through which a slow current of hydrochloric acid was transmitted, and when the contents of the boat had become liquid from the absorption of gas, a gentle heat was applied in order to distil over the chlorides of tin and antimony. When the distillation was nearly finished, a greater heat was used to expel the last traces of bichloride of tin, and, the tube having cooled, the boat was withdrawn, and its contents (chloride of lead) dissolved out, and added to the solution containing the nitrates of lead and copper. These two metals were determined as usual, the solution being evaporated nearly to dryness, with a slight excess of sulphuric acid, the sulphate of lead washed with water acidified with sulphuric acid, and the oxide of copper precipitated from the filtrate by a solution of potash. The chlorides of tin and antimony were poured into a small beaker; the apparatus rinsed out with dilute hydrochloric acid, and, after adding more hydrochloric acid, the solution was heated gently and digested with metallic iron (as pure as possible) until the whole of the iron had dissolved, cold water was then added, the antimony collected on a weighed filter, and after washing with cold water, dried at 110° C. The filtrate from the antimony, if not sufficiently dilute, was mixed with water, and then saturated with sulphuretted hydrogen. The sulphide of tin being afterwards converted into binoxide by ignition.

In order to simplify the process as much as possible, the following plan was eventually adopted. Ten grains or more

of the alloy to be analysed were introduced into a small piece of apparatus, having the following form, sufficient nitric acid to complete the oxididation was poured upon the alloy by means of a funnel-tube; the end *a* was corked, and the oxidation effected at a moderate temperature. When the alloy had been converted into a perfectly white mass, the excess of acid was expelled by attaching a tube and cork to *a*, and causing a gentle current of air to traverse the apparatus, either by means of an aspirator, or a pair of bellows; during this operation the apparatus should be heated sufficiently to cause the evaporation of the excess of nitric acid. The end *a* was now connected with an apparatus for generating dry hydrochloric acid (which should be made from fused chloride of sodium and sulphuric acid), while the end *b* was immersed in a small quantity of water contained in a beaker; the remaining part of the operation may be conducted as in the former process, care being taken not to distil the volatile chlorides too rapidly, and to avoid the fusion of the chloride of lead until all the bichloride of tin has been expelled.



The iron employed to precipitate the antimony should be in the form of thin sheet, about three times the weight of the antimony present, being usually sufficient for complete precipitation. It is necessary that the flask for generating the hydrochloric acid be provided with a funnel-tube, dipping just below the surface of the fluid, in order to prevent the too rapid absorption of the gas by the water which is used to condense the chlorides of tin and antimony.

LV.—*On the Composition of the Amorphous Deposit in Healthy Urine.*

By Professor Heintz, of Halle.

[Communicated in a letter to Dr. Bence Jones, F.C.S.]

In your paper on "The Composition of the Amorphous Deposits in Healthy Urine," at page 213, vol. xv., of the Journal of the Chemical Society, you state that I consider the deposit as a mixture of different acid urates, modified in form by the presence of other substances in the urine. I have nowhere said this. You will find my opinion founded upon my experiments at page 238 of Müller's Archives for 1845. I there say: "It is therefore certain that the amorphous sediment always contains urate of ammonia, urate of soda, and urate of lime, and more rarely urate of potassa and urate of magnesia;" and at page 260: "As I have already shown that the fine amorphous sediment consists of a mixture of urate of soda, urate of lime, and urate of magnesia, and that it has not only the same properties, but the same composition as the sediment prepared artificially, the cause of the natural sediment being deposited as a fine amorphous powder becomes very evident. This cause is the simultaneous precipitation of these three salts, one of which, the lime-salt, as I have shown in a former part of the paper, is always precipitated in the form of a fine amorphous powder, whilst the ammonia-salt and the soda-salt, when they are redeposited at the same time, from a solution containing common salt, frequently fall as a fine powder; but they more constantly form larger or smaller microscopic rounded masses."

You will see from this that I regard the simultaneous precipitation of the different uric acid salts as the cause of the formation of the amorphous deposit, and I do not consider that it depends on the presence of other substances in the solution.

I must add, however, that the misunderstanding you have fallen into is partly my own fault, inasmuch as I have not sufficiently distinguished in my paper the two kinds of amorphous sediments which are met with in the urine.

In the introduction I have only separated the crystalline sediment from the amorphous; although farther on I have divided

the latter into the fine granular deposit, easily soluble in warm water, and the larger rounded deposit, which is with difficulty dissolved in warm water. This last form I have often produced artificially when only the urates of soda and ammonia were present, whilst I obtained the finer granular form with certainty only when lime was present. I therefore stated that the presence of lime was necessary for the formation of the fine granular amorphous deposit of urates.

As oxalate has been so frequently found in the sediments of urine, subsequently to the date of my experiments, it might be thought that the lime which I obtained, came from this source; but, in opposition to this, I must say, first, that I sometimes filtered the fresh made urine before it gave the deposit of urates, and at other times that I redissolved the amorphous deposit, filtered it, and then took the sediment which fell on cooling for examination, and that then I always found lime present; and, secondly, that in forming artificially the fine amorphous deposit, the presence of lime was always necessary. But as you have found no lime in the sediments which you examined, it is evident that my conclusion, that lime is absolutely necessary for the formation of the fine amorphous deposit of urates, must be limited.

The sediments which you examined contained much potassa, and I found it only rarely, and then in very small quantity. I therefore made my experiments on the artificial production of the amorphous sediments with fluids free from potassa, and, under these circumstances, I found that it was essential that lime should be present. I must therefore restrict my conclusion thus, that for the formation of the fine amorphous powdery sediment, lime must be present if potassa is absent.

LVI.—*On a Volumetrical Process for the Analysis of Waters.*

By Edward Nicholson, F.C.S., Staff Assistant-Surgeon.

The want of a process by which surgeons and other scientific men interested in hygienic matters, could easily make an analysis of water, has long been felt; and attempts have several times been made to supply the deficiency.

Professor Clark, of Aberdeen, indicated the tincture of soap as a test for the presence of earthy salts in water; he adapted a burette, with a special graduation, to the determination of the hardness of water by the tincture of soap, and drew up a table for calculating the amount of the different earthy salts corresponding to the quantity of soap decomposed by the water.

The beautiful experiments of Professor Clark, after some examination and criticism by Professor Playfair, Mr. Campbell, and others, was adopted by MM. Boutron-Chalard and F. Boudet, as the basis of the so-called "Hydrotimétriè," for which a prize of 2,000 francs was awarded them by the Academy of Sciences. These chemists adapted the soap solution of Professor Clark to a more complete determination of the earthy bases, and as their very useful method has been used to some extent in France, and is employed in the Hygienic Laboratory of the Army Medical School at Fort Pitt, I will give a brief outline of the process they employ.

The solution of soap employed by MM. Boutron-Chalard and Boudet, is of such a strength, that 23 degrees of their burette (equal to 2·4 c.c.) form a permanent lather on agitation with 40 c.c. of a solution of chloride of calcium, containing 0·25 grm. per litre. One degree is deducted for the excess of soap-solution requisite to form the lather significative of the termination of the reaction. These 22 degrees correspond then to ·01 grm. of chloride of calcium, or to a quantity of any other soap-decomposing substance, varying according to the relation of its equivalent to that of chloride of calcium. The number of degrees of soap-solution decomposed by 40 c.c. of a water, when multiplied by certain factors, given in a table, gives the amount of chloride of calcium, or of any other salt, *ad libitum*, contained in the water.

The operations for the analysis of water by this method, comprise the following determinations:—

1. The hardness of 40 c.c. of water; this hardness is caused by carbonic acid gas, lime, magnesia, and whatever iron and alumina may be present.

2. The hardness of 40 c.c. of water from which the lime has been precipitated by oxalate of ammonia; this gives the hardness caused by magnesia and by carbonic acid gas.

3. The hardness of 40 c.c. of the water from which carbonate of lime and carbonic acid gas have been expelled by boiling; this *permanent* hardness, after a deduction of 3 degrees for carbonate

of lime still remaining in solution, is owing to salts of lime other than carbonate, and to salts of magnesia.

4. The hardness of 40 c.c. of the boiled water from which the *permanent* lime has been precipitated by oxalate of ammonia; this gives the magnesian hardness.

5. The sulphuric acid is estimated by adding to 40 c.c. of water, a measured quantity of solution of nitrate of baryta, of known hardness; the hardness of the mixture is determined, and the loss of hardness indicates the hardness of the sulphuric acid contained in the precipitated sulphate of baryta.

The distinguishing features in this improvement of Clark's process, are the estimation of the permanent lime and magnesia salts, and of the sulphuric acid.

This easy method of estimating the more important constituents of water render this process most valuable in the economical analysis of waters, as a means of determining the effect of a water on steam boilers and in domestic operations, and also as a method for calculating the exact amount of lime that must be added to water, to eliminate the carbonic acid and carbonate of lime. But, apart from its economical value, considering the process in the point of view of chemical analysis, it is liable to some objections, and appears susceptible of certain improvements.

Two of the determinations are made after the addition of oxalate of ammonia; and I find that this introduces a possibility of error, since the oxalate of ammonia, when added even in small excess, either gives a peculiar hardness of its own, or else deranges the production of a lather, so as to render the result uncertain. It is also impossible to express the exact constitution of the solid ingredients of the water, or give any precise idea of their composition. No account is taken of the alkaline salts, and thus the advantages of the method are not fully brought out.

Impressed with the delicacy of the reaction given by the solution of soap, with the minutest quantity of earthy base, or of carbonic acid gas (·00002 grm. of lime will cause a detectable hardness of 1-7th of a degree), I have endeavoured to adapt this delicate test to a more complete and reliable method of volumetrical analysis; and I believe I have succeeded in bringing the process of MM. Boutron and Boudet, by several modifications and additions, to an exactitude which leaves little to be desired. I have also simplified the calculations, so as to render them even easier than those necessary in ordinary gravimetrical analysis.

The burettes employed are divided into tenths of cubic centimetres or degrees, each 0·1 c.c. = 1°. These, with two pipettes of 10 c.c. and 50 c.c. respectively, a few basins and beakers, a few three-ounce stoppered bottles, and a graduated litre-measure, form all the apparatus required.

The following solutions are employed as test-fluids :—

1. *An Alcoholic Solution of Soap.*—The solution employed by MM. Boutron and Boudet is made with hard Marseilles soap, and in consequence it is solid at ordinary temperatures. This is a great inconvenience, from the necessity of heating the test-fluid; but, after experimenting on a considerable number of soaps, Dr. Parkes has found that the soft potash-soap of the London Pharmacopœia is the best; and this has accordingly been used by me. The solution is made by dissolving the soap, without heat, in a mixture of equal weights of alcohol and water.

The soap-solution is made of such a strength, that 20 degrees (2 c.c.) are exactly equivalent to 50 c.c. of a water containing 0·1 grm. per litre (or 7 grains per gallon) of carbonate of lime, and on adding to 50 c.c. of such a water 22 degrees, a permanent lather is produced by agitation. This requisite excess of 2 degrees per 50 c.c. is to be deducted from all determinations of hardness.

2. A solution of *nitrate of baryta,* containing 0·26 grm. per litre and equivalent in point of hardness to the aforesaid standard water containing 0·1 grm. per litre of carbonate of lime. 50 c.c. of this solution mark 20 degrees.

3. A stronger solution of *nitrate of baryta* is usually employed; it contains 1·300 grm. per litre; 50 c.c. of it mark 100 degrees.

4. A solution of *nitrate of silver* containing 8·500 grm. ($\frac{1}{20}$ of the equivalent of the salt) per litre.

5. A solution of *oxalate of ammonia,* containing 0·355 grms. ($\frac{1}{200}$ of the equivalent of the salt) per litre.

6. A solution of *permanganate of potash* containing 0·159 grm. $\frac{1}{1000}$ of the equivalent of the salt) per litre.

The above graduation of the solutions has been adopted, as the important advantage is thereby obtained, of being able to calculate the quantity of any substance per litre of water, by multiplying the number of degrees obtained by the atomic weights of the substance.

Thus—

20 degrees × 50 (eq. of $CaO.CO^2$) = ·1000 grm. per litre, of carbonate of lime.
20 degrees × 28 (eq. of CaO) = ·0560 grm. per litre, of lime.
20 degrees × 35·5 (eq. of Cl) = ·0710 grm. per litre, of chlorine.

The quantities thus obtained, when multiplied by 70, show the number of grains per gallon of water.

The Analytical Process.

1. 50 c.c. of the water to be analysed are measured by the pipette into a stoppered bottle of about three-ounce capacity. The soap-solution is gradually dropped in from the burette, the bottle being strongly shaken at intervals, until a lather begins to form on the surface. The soap-solution is then added more cautiously, and enough has been added, when the water, on agitation, presents an iridescent, large-bubbled lather, breaking down very slowly, and, after a few minutes, leaving the surface perfectly covered with a beady film, reconvertible into a lather on again agitating. After a little practice, the exact point where the lather becomes permanent is attained by the addition of one small drop, about one-sixth degree, of soap-solution. The process thus indicates the presence of ·0005 grm. per litre of lime.

Two degrees are deducted for the excess necessary to produce a lather. The number of degrees found represents the hardness due to lime, magnesia, iron, and carbonic acid gas. The alkaline salts usually found in water, have no effect on the soap-solution.*

2. The amount of *lime* and *magnesia*, and, by difference, of free *carbonic acid gas*, is found by taking the hardness of the water after expulsion of the carbonic acid gas. To this effect 50 c.c. of the water are evaporated to dryness with one or two drops of sulphuric acid, and the residue is ignited to expel excess of acid; if the vapours be offensive, the residue may be neutralized by a few drops of ammonia, before ignition. The residue is dissolved in 50 c.c. of distilled water, and the hardness is ascertained. Oxide of iron will remain insoluble; its amount is to be deducted from the carbonic acid.

3. The *lime* is determined by the well-known application of permanganate of potash to the oxidation of oxalic acid.

To 50 c.c. of the water, add 50 c.c. (or, if the hardness exceeds 50 degrees, 100 c.c.) of the standard solution of oxalate of ammonia, let the mixture stand in a warm place for an hour, and filter. The filtrate and washings are heated in a basin to about 70° C.,

* If the hardness exceed 80 degrees, or if much magnesia be present, the earthy soap often assumes a curdy form, deranging the production of a lather; in this case only 25 c.c. should be taken for experiment, the 50 c.c. being made up with distilled water.

with a few drops of hydrochloric acid, and the standard solution of permanganate of potash is added from a burette. Subtract the number of cubic centimetres of permanganate required for oxidation of the excess of oxalic acid, from the number of cubic centimetres of oxalate of ammonia added to the water: the difference gives the number of degrees of lime.

50 c.c. of the permanganate-solution ought exactly to oxidise 50 c.c. of the oxalate of ammonia-solution.

4. *Determination of the Alkalies.*—The amount of lime and magnesia once obtained by the processes described, the ordinary process of estimating the alkaline salts by evaporating a certain quantity of the water with sulphuric acid, and weighing the resulting sulphates, is much facilitated. The lime and magnesian hardness have merely to be multiplied by the equivalents of sulphate of lime and of sulphate of magnesia, and the numbers thus obtained to be deducted from the amount of mixed sulphates per litre of water. I have however devised the following method for the volumetrical determination of the alkaline salts:—

To 50 c.c. of the water, ignited with sulphuric acid, as before described (2),* add 20 c.c., or more, of the stronger solution of nitrate of baryta, taking care that the hardness of the quantity added (2 degrees per 1 c.c.) be much greater than that of the water, as previously ascertained. If no alkaline sulphates are present, the amount of sulphate of baryta precipitated will be exactly equivalent in hardness to the amount of earthy sulphates; and the hardness, when ascertained by the soap-solution, will be exactly that of the baryta-solution added. If, for example, 20 c.c. = 40 degrees of baryta-solution have been added to 50 c.c. of water containing 35 degrees of sulphate of lime and of magnesia (total 40 + 35), 35 degrees of sulphates of baryta will be precipitated and the hardness will be reduced to 40 degrees, exactly the hardness of the baryta added. But, on the other hand, if sulphate of soda be present in the water, in addition to the earthy sulphates, a greater quantity of sulphate of baryta will be precipitated, and the hardness will be reduced to less than 40 degrees. Should it be reduced to 36 degrees, that will show that 4 degrees of alkaline sulphate were present.†

* It may be as well, at process No. 2, to evaporat 200 c.c. of water with sulphuric acid, dissolve the ignited residue in 200 c.c. of distilled water, and take 50 c.c. for analysis.

† If 20 c.c. of baryta solution have been added, the excess of soap-solution, to form

5. The *chlorine* is determined in 50 c.c. of the water by the solution of nitrate of silver. If the quantity be very small, it is best to evaporate 500 c.c. of water to a small bulk, and count cubic centimetres as degrees.

6. The *sulphuric acid* is determined by adding to 50 c.c. of the water, 10 c.c., or more if necessary, of the stronger baryta-solution, and ascertaining by the soap-solution the hardness of the mixture. The loss of hardness from the precipitation of sulphate of baryta, gives the number of degrees of sulphuric acid.

7. *Iron* is determined in the usual manner by the permanganate of potash solution. 500 c.c. of the water are evaporated to a small bulk with hydrochloric acid; the iron is reduced by sulphurous acid, and estimated by the permanganate of potash solution. Ten cubic centimetres are counted as one degree of Fe^2O^3.

If silica be present, it will remain on redissolving the ignited sulphates, and if 200 c.c. of the water have been evaporated with sulphuric acid, it may be estimated by weighing.

In process 2, the oxide of iron becomes insoluble, and increases the amount of carbonic acid gas, from which it must be deducted.

All the processes here described are of very easy execution. The method of estimating carbonic gas is unequalled in exactness and facility of execution by any method I know, and the process for estimating the total capacity of saturation of the alkalies is extremely exact and satisfactory. The estimation of sulphuric acid, devised by M.M. Boutron and Boudet, is likewise of great precision.

I append examples of the calculation of an analysis performed by this process, to show the advantage obtained by the method of graduation I propose, in establishing an empirical formula for the salts contained in waters.

I. *Analysis of the Water supplied by the Chatham Water Company to Fort Pitt.*

	Degrees.	
1. Hardness	53°·7	Carbonic acid gas* Calcium ..... Magnesium .... Iron .....
2. Hardness after ignition with sulphuric acid ..	49°·7	Calcium ..... Magnesium ....
3. Calcium ascertained by permanganate	48°·3	Calcium .....

a lather, will be greater; 2·8 degrees must be deducted. But it is perhaps better always to add 50 c.c. (100 degrees) of baryta. The deduction is then 4 degrees, and the loss of hardness on 100 degrees is the amount of alkali.

* The iron is to be deducted from the gross carbonic acid, 4 degrees.

	Degrees.	
4. Hardness after ignition with sulphuric acid, solution, and 60 degrees of baryta added	53°·6	(Sodium loss 6°·4)
5. Chlorine	5°·5	.....
6. No sulphuric acid		.....
7. Iron	0°·2	.....

Deduction of an Empirical Formula for the Salts contained in the above Water.

This calculation, so tedious by the ordinary method, becomes here of extreme simplicity. I combine the 5·5 degrees of chlorine with an equal number of degrees of sodium, a balance of ·9 degrees of sodium is left. This with the calcium and magnesium is calculated as carbonate.

	Deg.	Equivs.		Grm.	per litre.	Grs. per gal.
Carbonate of lime ..	48·3	× 50	=	·2415	× 70 =	16·905
Carbonate of magnesia	1·4	× 42	=	·0058	× 70 =	·406
Carbonate of soda....	·9	× 53	=	·0047	× 70 =	·329
Chloride of sodium ..	5·5	× 58·5	=	·0321	× 70 =	2·247
Oxide of iron.....	·2	× 80	=	·0016	× 70 =	·112
Silica			=	·0020	× 70 =	·140
				·2877		20·139
Carbonic acid gas	3·8	× 44	=	·0167	=	= 2·52 c.
	($2CO^2$)			8·93c.c.		in per gal.
Residue on ignition.....				·2810		= 19·68.

II. *Water from a pump at Fort Pitt.*

	Degrees.
Total hardness	36·8
Calcium and magnesium	21.0
Calcium	16·9
Sodium	5·0
Iron (Fe^2O^3)	1·2
Sulphuric acid	4·8
Chlorine	3·6

	Degrees.		Grm. per litre.	Grains per gal.
Carbonate of lime	16·9 × 50		= ·0845 × 70	= 5·915
Carbonate of magnesia	·7 × 42		= ·0029 × 70	= ·203
Carbonate of iron	1·2 × 116	$2(FeO,CO^2)$	= ·0139 × 70	= ·973
Sulphate of magnesia.....	3·4 × 60		= ·0204 × 70	= 1·428
Sulphate of soda.....	1·4 × 71		= ·0099 × 70	= ·693
Chloride of sodium.....	3·6 × 58·5		= ·0210 × 70	= 1·470
			·1526	10·682.
Carbonic acid gas	14·6 × 44		= ·0642	= 31·3c.c. pr. lit.
			(× ·537)	(31.3 c.c. × 4·54 × ·061)
Solids by evaporation ·1500 per litre.				= 8·67c. in. per gallon.

I may mention that the solution of permanganate of potash, of the standard here employed, answers admirably for the estimation of organic matter in water. 500 c.c. of water are heated to 70°C., with a few drops of pure sulphuric acid, and the standard solution is added, 1 c.c. at a time, until a colour, lasting for 10 minutes, is obtained. Every 10 c.c. of test-solution thus decolorised is equal to one degree of organic matter requiring one equivalent of oxygen for complete oxidation (corresponding to C^2O^3,HO, for example).

I may say a few words as to the best manner of attaining the rapidity which forms one merit of this process. I first set 200 c.c. of water to evaporate with a few drops of sulphuric acid for processes 2 and 4; I also precipitate the lime in 50 c.c. for process 3. By the time I have taken the total hardness, and estimated the chlorine, sulphuric acid and iron, the evaporation is finished and the residue ready to be taken in hand. Two or three analyses can thus be easily performed in a day. One point must be carefully observed: that the distilled water contain no carbonic acid gas. The delicacy of the soap-test for this gas is so great that the distilled water will speedily acquire one or two degrees of hardness, if left exposed to the air. If it has acquired any hardness from this cause, it should be boiled previously to use.

In conclusion I must beg to acknowledge my obligations to Dr. Parkes, who, by his discovery of the fact, that, contrary to expectation, potash-soap might be employed to make a soap solution perfectly fluid at ordinary temperatures, removed what would have been an insuperable bar to any perfection of the method of analysis.

LVII.—*On Hypobromous Acid.*

By William Dancer,

Dalton Scholar in the Laboratory of Owens College, Manchester.

Balard* in his original memoir on bromine, published in 1826, mentions that when bromine water is brought into contact with the alkalies and alkaline earths, dissolved or suspended in water, the smell and colour of the bromine disappear, whilst no oxygen gas is evolved, and that, on the addition of a weak acid to the solution, bromine is liberated; a reaction, observes Balard, which proves that bromine forms with these oxides a compound analogous to the so-called chlorides of lime and soda.

Many other chemists, especially Löwig,† Fritsche,‡ and Gay Lussac,§ mention the mode of preparing a bleaching salt of bromine with the alkalies, indicating the existence of hypobromous acid; indeed Gay Lussac states that this oxide can be obtained in the gaseous state by the action of bromine on dry oxide of mercury, but Pelouze showed that the gas thus produced was oxygen. Our knowledge concerning the properties of this oxide of bromine is, however, very limited, so much so that Berzelius states that even its existence is uncertain.

At the suggestion of Professor Roscoe, I undertook the investigation of this subject, and I have succeeded in establishing the composition of hypobromous acid in aqueous solution, and in determining some of its properties.

I have, however, been unable to prepare the hypobromous anhydride, as this body is far more unstable than the corresponding chlorine compound, and when liberated in the gaseous form, splits up, even at the ordinary atmospheric temperature, into bromine and oxygen.

In order to assure myself of the absence of chlorine in the bromine employed, the whole quantity of bromine was dried and distilled; the first portion of the distillate was collected separately, and a weighed quantity of this liquid reduced by aqueous sulphurous acid, and precipitated as bromide of silver; thus 2·3345 grms. of bromine yielded 5·486 grms. of bromide of silver, the theoretical

* Ann. Ch. Phys., xxxii. 337.
† Pogg. Ann. xiv. 14, 485.
‡ J. pr. Chem., xxiv. 291.
§ Compt. rend., xiv. 951.

weight of silver-salt obtainable from the above quantity of bromine being 5·487 grms. A second analysis was made by passing dry chlorine gas over a weighed portion of bromide of silver obtained from a similar quantity of bromine; 2·294 grms. of bromide of silver yielded 1·755 grm. of chloride of silver, a quantity closely corresponding to the theoretical amount of 1·751 grm. Hence we may conclude that the bromine employed was free from chlorine.

I.—*Action of Bromine on Aqueous Solutions of the Salts of the Alkalies and Alkaline Earths.*

(1). On shaking a strong solution of hydrate of potash or soda with bromine, no bleaching compound is formed, bromide and bromate of potassium only being produced.

(2). With a weak solution of hydrate of potash or soda, a slightly yellow liquid is obtained, which bleaches strongly; this must contain a compound of the alkali with hypobromous acid, as upon distillation, either under the ordinary atmospheric pressure, or *in vacuo*, the distillate does not possess bleaching properties, and becomes slightly coloured with free bromine.

(3). On shaking bromine-water with solution of the carbonate of potassium or sodium, carbonic acid is given off, and the liquid, which is of a light yellow tint, bleaches vegetable colours. On being heated to 30°C., or left for some time at the ordinary atmospheric temperature, bromine is liberated, and the solution becomes colourless, losing its bleaching properties.

(4). When an aqueous solution of phosphate of sodium is shaken up with bromine-water, a bleaching solution is produced; this, however, cannot be distilled even *in vacuo* without decomposition, free bromine being evolved.

(5). Bromine shaken up with solution of chloride of sodium does not yield a solution containing hypobromous acid, behaving with this salt unlike chlorine, which, according to Williamson, yields a solution from which free hypochlorous acid can be obtained by distillation.

(6). Solid hydrate of lime shaken up with bromine, absorbs it with evolution of heat, becoming coloured red. If a small quantity of water be added, the mixture gradually loses its colour, and gains the peculiar sweetish smell of bleaching powder; filtered from the excess of lime, the solution has a light yellow colour, and bleaches vegetable colours rapidly.

This solution, even when very weak, is decomposed by dilute nitric, sulphuric, and hydrochloric acids, behaving with these acids unlike the corresponding chlorine compound. Carbonic anhydride in excess, when passed into strong solutions, decomposes this salt, liberating bromine; but when this gas is passed slowly into a dilute solution, the hypobromous acid is not entirely decomposed, for on distilling *in vacuo* the distillate was found to contain hypobromous acid, as well as free bromine.

(7). Bromine water added to baryta-water partially loses its colour, and the solution possesses strong bleaching properties. A current of carbonic anhydride passed through the solution liberates bromine, and after some time precipitates the barium as carbonate. Hence it is evident that bromine forms with baryta compounds similar to those which it forms with lime.

II.—*Action of Bromine-water on Solution of Nitrate of Silver.*

When pure bromine-water is shaken up with excess of nitrate of silver solution, a liquid is produced which bleaches strongly (Spiller *). This liquid, on boiling, yields a distillate, of which the first portions contain much free bromine, but the later portions possess a light straw-colour, and still bleach vegetable colouring matters powerfully. If the distillation of the solution be conducted *in vacuo* under a total pressure of 50 mm. of mercury, the liquid boils at 40°C.; and all the distillates have a straw colour; they do not contain free bromine, they possess an acid reaction, and bleach strongly. If, however, the temperature rises to 60°C., the dark-coloured vapour of bromine appears in the retort, showing that at that temperature decomposition of the hypobromous acid ensues.

For the purpose of determining the composition of the bleaching substance here present, definite volumes (50 cbc.) of the almost colourless acid distillate were completely reduced with freshly prepared solution of sulphurous acid, and the excess of sulphurous acid was removed by rapid boiling. In one of the portions, the sulphuric acid formed was estimated as barium-salt; in the other the barium weighed as bromide of silver.†

For every 233 parts by weight of sulphate of barium obtained, the liquid contained 8 parts by weight of oxygen; out of every 188 parts of bromide of silver found, 80 parts of bromine were com-

* Chem. News, 1, 38.

† According to the method proposed by Calvert and Davies for the analysis of hypochloric acid.—Chem. Soc. Journ., vol. ii., p. 193.

bined with this oxygen. Hence the relation between the quantities of bromine and oxygen in the compound is obtained.

The following numbers give the experimental results, and show that bromine and oxygen are contained in the liquid in quantities represented respectively by the numbers 80 and 8 :—

I.—50	cbc. of distillate yields	0·402	grms.	$BaSO_4$	and	0·324	grms. AgBr.
II.—50	"	"	0·222	"	"	0·183	"
III.—50	"	"	0·417	"	"	0·321	"
IV.—60	"	"	0·389	"	"	0·323	"

Hence—

	Calculated.		Found.			
			I.	II.	III.	IV.
Br	80·0	90·91	90·90	91·07	90·53	91·13
O	8·0	9·09	9·10	8·93	9·47	8·87
	88·0	100·00	100·00	100·00	100·00	100·00

In order to determine whether half the total bromine in contact with nitrate of silver solution, is converted into hypobromous acid, two equal volumes of the same bromine water were taken, and in one portion the total bromine was determined after complete reduction with sulphurous acid, whilst to the other portion nitrate of silver was at once added, and the precipitated bromide of silver was weighed.

1. 50 cbc. Bromine-water reduced with sulphurous acid, yielded 1·206 grms. BrAg, or 0·513 Br.

50 cbc. Bromine-water not reduced with sulphurous acid, yielded 0·647 grms. BrAg, or 0·275 Br.

Hence 46·40 per cent. of the total bromine was contained in the form of hypobromous acid, and was not precipitable by nitrate of silver.

2. 50 cbc. Bromine-water reduced with sulphurous acid yielded 1·618 BrAg, or 0·6885 Br.

50 cbc. Bromine-water not reduced with sulphurous acid yielded 0·957 BrAg, or 0·4072 Br.

Hence 40·88 per cent. of the total bromine was contained in solution as hypobromous acid.

3. 50 cbc. Bromine-water reduced with sulphurous acid yielded 1·205 BrAg, or 0·5126 Br.

50 cbc. Bromine-water not reduced with sulphurous acid yielded 0·642 BrAg, or 0·273 Br.

Hence 46·74 per cent. of the total bromine was contained in solution as hypobromous acid.

On standing in contact with excess of nitrate of silver solution, aqueous hypobromous acid is slowly decomposed, and bromide of silver is precipitated; this explains the excess of bromide of silver found in the unreduced portions. From the above analyses it is however clear, that the decomposition in question really occurs.

On distillation at temperatures above 60°C., aqueous hypobromous acid is decomposed, free bromine being liberated and bromic acid formed. This is shown by the appearance in the retort of a difficultly soluble silver-salt, which crystallised in long needles, and was shown by analysis to be bromate of silver

III.—*Action of Bromine-water on Oxide of Mercury.*

Hypobromous acid is likewise formed when bromine-water is shaken up with finely divided protoxide of mercury, prepared either by igniting the nitrate, or by precipitation with potash.

After agitation for a short time with an excess of oxide of mercury, the whole of the bromine disappears; no oxygen gas is evolved, but the liquid assumes a light straw colour, possesses the peculiar sweetish smell characteristic of hypobromous acid, and bleaches strongly. This liquid when distilled under the ordinary atmospheric pressure, undergoes rapid decomposition; free bromine is given off in large quantities, and bromate of mercury remains behind in the retort. Under a pressure of 40mm. of mercury, when the liquid boils at about 30°C., the aqueous hypobromous acid distils over undecomposed.

By saturating aqueous hypobromous acid, thus prepared, with bromine, shaking again with oxide of mercury, and repeating these operations several times, a more concentrated aqueous solution of hypobromous acid can be obtained; 100 cbc. of a liquid which had been thus treated six times, was found to contain 6·21 grms. of combined bromine in solution. It is not possible, however, to obtain a pure distillate from a liquid prepared in this way, as the concentrated solution is decomposed even at 30° C., bromine being liberated in large quantities.

That the hypobromous acid, like the corresponding chlorine compound, is not combined with the oxide of mercury, is proved by the fact of its volatility. Owing, however, to the ease with which this body splits up into bromine and bromic acid, the hypobromous acid obtainable in the distillate is not equivalent

to half the total quantity of bromine employed. In one experiment, 1,000 cbc. of bromine-water containing 10·44 grms. bromine, yielded on distillation only 2·818 grms. of bromine combined as hypobromous acid. In this respect, then, the lowest oxide of bromine differs from aqueous hypochlorous acid, which, as Gay Lussac showed, may be distilled when dilute, without any decomposition occurring.

The first portions of the distillate contain, however, by far the largest proportion of the acid, as is shown by the following determinations:—

1. 1,000 cbc. of bromine-water, containing 16·88 grms. of bromine, were shaken up with oxide of mercury, and the clear liquid distilled in vacuo at 30°C., under a pressure of 40 mm. mercury. Successive volumes of the distillate, amounting to 100 cbc. each, were analysed with standard silver-solution after complete reduction with sulphurous acid.

The 1st	100 cbc.	contained	0·736	grms.	bromine.
2nd	„	„	0·560	„	„
3rd	„	„	0·404	„	„
4th	„	„	0·304	„	„
5th	„	„	0·244	„	„
6th	„	„	0·174	„	„
7th	„	„	0·156	„	„
8th	„	„	0·080	„	„

2. 1,000 cbc. of bromine-water, containing 10·00 grms. bromine, treated with oxide of mercury and distilled, gave the following results:—

The 1st	100 cbc.	contained	0·416	grms.	bromine.
2nd	„	„	0·404	„	„
3rd	„	„	0·240	„	„
4th	„	„	0·124	„	„
Mean of the 5th, 6th, 7th	„	„	0·113	„	„
8th	„	„	0·024	„	„

In order to determine the proportion of the total quantity of bromine which, in contact with oxide of mercury and water, formed hypobromous acid, a solution of bromine-water, containing in 25 cbc. 0·2537 grms. of bromine, was shaken up with an excess of oxide of mercury until all the free bromine had disappeared; the solution was then filtered, and the mercury in the filtrate

estimated as sulphide; 0·211 grms. of sulphide of mercury corresponding to 0·1455 grms. bromine, was obtained. In like manner, the filtrate from 100 cbc. of a second portion of bromine-water, containing 1·797 grms. of bromine, yielded 1·6365 grms. of sulphide of mercury, corresponding to 1·128 grms. of bromine. Hence it appears that in the one case 42·64 per cent. of the total bromine was converted into hypobromous acid, and in the other case 37·22 per cent. It is probable that a soluble salt of mercury and hypobromous acid is thus formed; this supposition would, at least, account for the excess of mercury found in the filtrate.

The extremely unstable character of the aqueous hypobromous acid, at the ordinary atmospheric temperature, is well shown by its behaviour with oxide of silver. When bromine water is agitated with finely divided oxide of silver in excess, hypobromous acid is immediately produced, and if the solution be quickly poured off from the excess of oxide and from the precipitated bromide which is formed, it possesses strongly bleaching properties; but if it be allowed to remain, even for a few minutes, in contact with the excess of oxide of silver, bubbles of oxygen gas are given off, bromide of silver is formed, the solution becomes colourless, and altogether loses its bleaching power. It is probable that hypobromite of silver exists in this solution; for if the solution, poured off quickly from the excess of oxide of silver, be allowed to stand for some time, it is found to decompose, bromide of silver being precipitated.

IV.—*Action of Bromine upon dry Oxide of Mercury.*

On acting with bromine upon an excess of dry oxide of mercury, prepared by igniting the nitrate, great heat is evolved; and, if the mixture be heated in a sealed tube at 100° C., a dry powder is formed which possesses the peculiar smell of bleaching-powder, and, when treated with water, gives a strongly bleaching solution. No bleaching substance is, however, formed when an excess of bromine is employed, a hard mass remaining in the tube, but in both cases large quantities of oxygen gas are liberated, causing the tubes to burst with a loud noise when the ends are opened with a file. The mercury, bromine, and oxygen contained in a portion of the powder from one of these tubes, were determined directly.

(a). *Determination of Bromine.*—1·1295 grms. of the mass left in the tube, was dissolved in nitric acid, and the bromine pre-

cipitated with nitrate of silver, 0·7195 grms. bromide of silver was obtained, corresponding to 27·11 per cent. bromine.

(b). *Determination of Mercury.*—1·1335 grms. of the same mixture was dissolved in hydrochloric acid, and the mercury precipitated by sulphuretted hydrogen, 0·8975 grms. HgS was obtained, corresponding to 68·28 per cent. mercury.

(c). *Determination of Oxygen.*—0·9575 grms. of the mixture was placed in a combustion-tube, closed at one end, containing some dry carbonate of manganese; after the air had been expelled from the tube by heating the carbonate, the mercury-salt was heated and the oxygen-gas collected over mercury; the apparatus was again swept out by the carbonic acid, and after this gas had been removed from the receiver by solution of caustic alkali, the oxygen was transferred to a calibrated eudiometer for measurement, care being taken to ensure the complete removal of the carbonic acid, by means of a potash ball. The volume of oxygen thus obtained reduced to 0°C. and 760 mm. Bar., amounted to 256 cbc., corresponding to 3·84 grms. in 100 grms. of the mixture.

From these data, the relative quantities of bromide of mercury, oxide of mercury, and hypobromite of mercury present in the mixture, can be calculated by the help of the three following equations:—

Let x equal the per centage weight of HgBr in salt.
y „ „ „ HgO „
z „ „ „ HgOBrO „

(1). $\frac{100}{280}x + \frac{100}{108}y + \frac{100}{196}z = 68{\cdot}28$

(2). $\frac{80}{280}x + \frac{80}{196}z = 27{\cdot}11$

(3). $\frac{8}{108}y + \frac{16}{196}z = 3{\cdot}84$

Or $x = 48{\cdot}62$ per cent. bromide of mercury.
$y = 37{\cdot}06$ „ oxide „
$z = 13{\cdot}48$ „ hypobromite „

99·16

Another portion of the bleaching salt was prepared, and analysed as before. The following results were obtained:—

(1). 0·869 grms. gave 0·3735 grms. BrAg = 18.29 per cent. bromine.

(2). 0·871 grms. gave 0·7545 grms. HgS = 74·64 per cent. mercury.

(3). 1·688 grms. gave 588·3 cbc. O at 0°C. and 76 mm. = 5·00 per cent. oxygen.

Hence by substituting these numbers in the foregoing equations we have—

x =	31·50	per cent.	bromide of mercury.
y =	55·89	„	oxide „
z =	10·54	„	hypobromite „
	97·93		

A portion of the contents of the tubes consisting of a hard solid mass was separated from the adhering powder, and analysed. This, as is seen by the following numbers, consists of a mixture of bromide and oxide of mercury, the former existing as a white crust surrounding the latter, the hypobromite in this portion having been probably decomposed either by the heat which was evolved during combination, or by an excess of bromine.

(1). 1·8355 grms. of the salt gave 1·032 grms. BrAg, corresponding to 23·92 per cent. of bromine.

(2). 1·644 grms. of salt gave 1·389 grms. HgS, corresponding to 72·85 per cent. of mercury.

(3). 1·782 grms. gave 399·5 cbc. of oxygen, at 0°C. and 76 mm., corresponding to 3·22 per cent. of oxygen.

Hence it is seen that the solid substance consisted simply of a mixture of bromide and oxide of mercury in the following proportions :—

Bromide of mercury	=	56·25	per cent.
Oxide „ „	=	46·36	„
		102·61	

V.—*Attempts to Prepare Hypobromous Anhydride.*

All the methods used for obtaining hypochlorous anhydride fail when applied to produce the corresponding bromine compound. When dry chlorine is passed slowly over dry oxide of mercury, gaseous hypochlorous anhydride is formed. When, however, the same reaction is repeated with bromine, no hypo-

bromous anhydride is formed, oxygen gas alone being produced, both at the ordinary atmospheric temperature, at 100°C., and at minus 18° C.

When bromine acts upon moist oxide of mercury, no oxygen gas is evolved, but the hypobromous acid is all absorbed by the water, and if the mixture be heated to a temperature above 30°C., it is decomposed, bromic acid and free bromine being the products.

The method used by Balard for preparing hypochlorous anhydride, by placing a saturated aqueous solution of the acid in a tube over mercury, and absorbing the water with nitrate of lime or phosphoric acid, does not give satisfactory results with hypobromous acid, for the strong aqueous acid is decomposed in contact with the mercury, and the gas which collects proves to be oxygen. The spontaneous decomposition of gaseous hypobromous anhydride, at the ordinary atmospheric temperature, into bromine and oxygen, was shown in the following manner:— About two ounces of oxide of mercury, together with six ounces of water, were put into a flask, half an ounce of bromine was added, and the whole well shaken up; as soon as the solution had lost its red colour, another portion of bromine was added, and it was again well shaken. This process was repeated (more oxide of mercury being occasionally added), until about five ounces of bromine had been used; the liquid, which did not smell of free bromine, was then filtered, and a small flask was completely filled with it, and this flask was connected by means of a piece of caoutchouc tubing (containing a Bunsen-valve), with a large bulb blown upon a thick piece of glass tube; the connections being made good, the bulb was attached to the air pump, exhausted, and the tube sealed off between the bulb and the air pump. When the valve between the exhausted bulb, and the flask was opened, gas possessing the colour of bromine was given off from the liquid, even at the ordinary temperature. After a short time the bulb was opened under water, no apparent absorption took place. Another bulb filled in a similar way, was opened under mercury, in a few minutes the gas became colourless, and the mercury rose in the tube. An eudiometric analysis was made of the residual gas, and the following results were obtained:—

No. 1. Analysis of gas evolved at the ordinary atmospheric temperature, and under reduced pressure.

	Vol.	P.	Temp.	Vol. at 0° and 76 mm.
Volume of gas employed.....	206·5	332·5	18·5	80·63
Ditto after addition of hydrogen ..	311·9	438·5	14·8	165· 9
Ditto after explosion	246·2	362·0	12·6	107· 3

The oxygen which remains, after deducting the calculated quantity required to form air with the nitrogen present, amounts to 3·26 per cent.

No. 2. Analysis of gas evolved at 25°C., and under reduced pressure.

	Vol.	P.	Temp.	Vol. at 0°C and 760 mm.
Volume of gas employed.....	191·87	324·7	9·0	77·34
Ditto after addition of hydrogen ..	389·06	514·2	9·5	250·10
Ditto after explosion	340·78	460·5	7·3	197· 7

The surplus oxygen in this case amounts to 1·7 per cent. From this it is seen that the gas consisted of a mixture of air, oxygen and bromine, the two latter resulting from the decomposition of the hypobromous anhydride.

VI.—*Solubility of Bromine in Water.*

To the above experiments I have to add the following determinations of the solubility of bromine in water between 5° and 30°C. The numbers in the first column of the following table give the temperatures at which the solubility was determined; the numbers in the second column give the weight of bromine in grammes contained in 100 grms. of bromine-water at the corresponding temperature as the mean of several estimations:—

No.	I.	II.
1	5°C	3·600 grms.
2	10°	3·327 „
3	15°	3·226 „
4	20°	3·208 „
5	25°	3·167 „
6	30°	3·126 „

By help of graphical interpolation, the following numbers were obtained for the solubility of bromine in water between 5° and 30°C :—

Temp.	Bromine in 100 Bromine-water.	Temp.	Bromine in 100 Bromine-water.	Temp.	Bromine in 100 Bromine-water.	Temp.	Bromine in 100 Bromine-water.
5°C	3·600	13°	3·269	21°	3·186	29°	3·136
6	3·536	14°	3·253	22°	3·179	30°	3·131
7°	3·474	15°	3·236	23°	3·173		
8°	3·421	16°	3·228	24°	3 166		
9°	3·376	17°	3·218	25°	3·159		
10°	3·336	18°	3·208	26°	3·151		
11°	3·313	19°	3·200	27°	3·146		
12°	3·229	20°	3·192	28°	3·141		